Resonant vibrations, peak broadening and noise in single molecule contacts: beyond the resonant tunnelling picture

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(Dated: October 15, 2010)

We carry out experiments on single-molecule junctions at low temperatures, using the mechanically controlled break junction technique. Analyzing the results received with more than ten different molecules the nature of the first peak in the differential conductance spectra is elucidated. We observe an electronic transition with a vibronic fine structure, which is most frequently smeared out and forms a broad peak. In the usual parameter range we find strong indications that additionally fluctuations become active even at low temperatures. We conclude that the electrical field feeds instabilities, which are triggered by the onset of current. This is underscored by noise measurements that show strong anomalies at the onset of charge transport.

PACS numbers: 85.65.+h, 72.10.Di, 73.23.-b, 73.40.Gk, 63.22.-m, 81.07.Nb

We consider charge transport across single conjugated molecules. The fundamental picture to understand the current voltage characteristics is the resonant tunnelling model [1, 2]. At low bias, no charge transport occurs due to the absence of a resonant level and Coulomb blockade. In lowest order, current starts to flow at a certain threshold, at which the electrons are energetically allowed to occupy an orbital in the molecule. The consequence is a step-like increase of the current $I(V)$, or correspondingly a peak in the differential conductance $\mathrm{d}I/\mathrm{d}V(V)$. In the framework of a pure electronic transition, it is well known that the peak width of the differential conductance is determined by the temperature T and the coupling constant Γ. We have measured more than ten molecular species and none of them showed correspondingly narrow peaks at the onset of conductance, even at low temperatures (significantly smaller than 10 mV, in contrast to the observed 100-300 mV). Hence there is a qualitative mismatch between the purely electronic resonant tunnelling model and experimental data: the peaks appear by far too broad.

This is partially resolved when vibrations are considered [3]. Their impact on IV characteristics is expected to be inelastic sidepeaks to the electronic peaks. Such signatures have been resolved in rather few experiments, where the first peak is explicitly tuned towards low bias voltages (< 100 meV) by an external gate [4–6], only in rare cases without an external gate [7]. However, it is not obvious how many and which vibrational modes are excited and show up as additional transport channels in the differential conductance. Equidistant peaks have been observed [7] which indicate a fundamental vibrational excitation and its higher harmonics. Theory shows that a single vibronic mode can trigger a bunch of excitations [8]. Additionally, dynamic behavior of electron transport is not only driven by vibronic excitations, but also by fluctuation processes due to instabilities in the contact configuration [9]. In the following we show that the resonant tunnelling model (including vibrations) is suitable for the description of the first peak only at small voltages. We show further deviations from this model, which are associated to bias-induced fluctuations.

We use the mechanically controlled break junction (MCBJ) technique. The method is desribed elsewhere [10]. The features discussed here have been found to be general for several (> 10) organic compounds. They all have a delocalized π-electron system and a length of about 2 nm, some of them containing at least one metal ion center. As an example, the molecule Fe^{2+}-bis(pyrazolyl)pyridine [11] is used for the measurements presented in the figures 1, 3 and 4 and an oligo(phenylene vinylene) (OPV-3) molecule in the figure 5.

We first turn our attention to the low-voltage regime. Typically the first conductance peak occurs at some hundred millivolts. However, this value varies substantially from junction to junction as a consequence of the uncontrolled local environment [10]. In few junctions, the onset of current occurs at few tens of millivolts. Here, the expectations from the resonant tunnelling picture are well fulfilled and a closer look elucidates the physics of the first peak.

A measurement of current and voltage in figure 1, taken with a resolution of 0.5 mV per step reveals a substructure in the general peak form. Several peaks appear on a background of a rather large peak structure.

We analyze the equidistant fine structure and find that the peak separation at negative and positive bias voltages has a ratio of $8.3/5.2 = 1.6$. Correspondingly, the onset of current has the same ratio of $|-43.2/28.0| = 1.6$. This can readily be explained by a molecular electronic level that is accompanied by vibronic levels at intervals of $\hbar\omega$ and coupled asymmetrically to the electrodes, as illus-

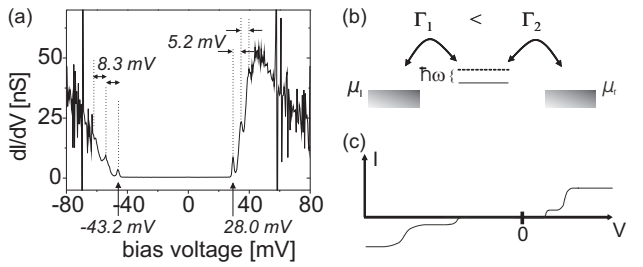

FIG. 1: (a) $\mathrm{d}I/\mathrm{d}V$ measurement at the first electronic peak for a small blockade region. Several single excitations can be recognized, for positive voltages the distance is $\approx 5.2\,\mathrm{mV}$, for negative $\approx 8.3\,\mathrm{mV}$. The onset of current shows the same asymmetry, taking place at $-43.2\,\mathrm{mV}$ and at $+28.0\,\mathrm{mV}$. (b) Schematic representation of two leads with chemical potentials μ_l and μ_r coupled asymmetrically ($\Gamma_1 > \Gamma_2$) to a molecular level, which is accompanied by a vibrational state $\hbar\omega$. (c) Resulting current-voltage characteristic. The onset of current and peak distance is lower for positive voltages at the weaker coupled left electrode (in case of LUMO-transport).

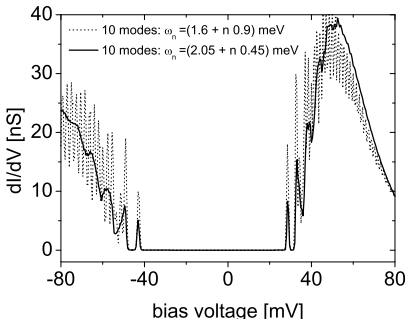

FIG. 2: $\mathrm{d}I/\mathrm{d}V$ characteristics obtained from a nonequilibrium Green's function calculation for a resonant level model [8, 12, 13]. The model comprises an electronic state 39 meV above the system's Fermi-energy and ten vibrational modes with frequencies ω_n that are coupled to this state with a uniform coupling strength such that the reorganization energy amounts 22 meV for both plots. In the calculation, the vibrational modes are assumed to be in their thermal equilibrium state determined by the junction's temperature $T = 1\,\mathrm{K}$. The level-width functions $\Gamma_1 = 13\,\mu\mathrm{eV}$ and $\Gamma_2 = 9\,\mu\mathrm{eV}$ have been chosen to model the current and voltage drop retrieved from figure 1a.

trated in Fig. 1b. The asymmetry creates asymmetric voltage drops at the two molecule-metal interfaces. So in one voltage direction the molecular levels will be in resonance at smaller absolute voltages, and also the peak separation will be larger if the stronger coupled electrode moves along the levels. This leads to a current-voltage characteristic as plotted in Fig. 1c. The onset of current and the peak separation at both polarities fulfill the same relation as the coupling to the electrodes, if the voltage drop is assumed to satisfy the same ratio.

A vibrational excitation energy of $E_\mathrm{vib} \approx 3.2\,\mathrm{meV}$ can be extracted. This qualitatively fits to the spectrum of vibrational modes that are obtained from DFT-calculations (BP86/def-TVZP) for the free molecule. For example, there are thirteen modes with frequencies in the range of 0.8 meV to 10 meV.

In principle, the observed peak shape can be modelled within the resonant tunnelling model, assuming electronic-vibrational coupling to a multitude of vibrational modes. As an example, figure 2 shows results of nonequilibrium Green's function model calculations [8, 12, 13], which reproduce the experimental data in figure 1a rather well. The underlying model includes a single electronic state on the molecular bridge, located 39 meV above the Fermi-energy, which is coupled uniformly to ten harmonic vibrational modes (with a corresponding reorganisation energy of 22 meV for both plots). The frequencies of the vibrational modes are chosen as $\omega_n = 2.05 + n\,0.45\,\mathrm{meV}$ and $\omega_n = 1.6 + n\,0.9\,\mathrm{meV}$ for the black and the red line, respectively ($n \in \{1..10\}$).

In agreement with the experimental data, the model calculations predict a broad peak in the conductance. It is emphasized that the width of this peak is not related to molecule-lead coupling ($\Gamma_{1/2} \approx 0.01\,\mathrm{meV}$) or thermal broadening ($k_\mathrm{B}T \approx 0.1\,\mathrm{meV}$) but is a result of the coupling to the distribution of vibrational modes and is approximately determined by the overall reorganization energy of 22 meV. A more detailed analysis of the conductance reveals a complex substructure, the details of which depend on the specifics of the model [12]. The first narrow peak appears once the chemical potential in one of the leads allows the population of the resonant level. At larger bias voltages the single conductance-peaks overlap with each other and form a broad peak. The small gap between the first narrow peak and the following broadened structures is determined by the frequency ω_1. It is noted that vibrational relaxation processes, e.g. due to coupling to phonons in the gold contacts, as well as anharmonic effects, which are neglected in the present calculation, will result in a further broadening of the peak structures.

Although the calculations within the resonant tunnelling model show that the observed peak structure can be explained in principle, our experiments give also information that supports a more complex physics. With the MCBJ technique, we are able to stretch stable junctions. Microscopically, we expect that the gold tip is further pulled out, which results either in a deformation of the contact bonds and/or in a reduction of the self capacitance of the molecular junction. Experimentally, this goes along with an enlargement of the blockade region in $\mathrm{d}I/\mathrm{d}V(V)$. Hence, the first peak occurs at higher voltages. When the junction is further stretched, a sudden reorganisation of the contact or a disruption may occur. We recorded current-voltage characteristics at four successive positions (see Fig. 3). Considering

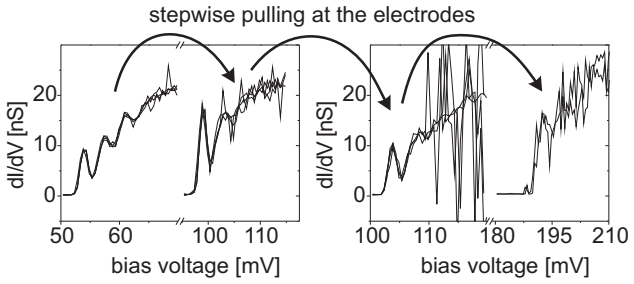

FIG. 3: dI/dV measurements at the onset of current for a small blockade region (left curve) and after pulling at the electrodes in three subsequent steps. With increasing onset voltage the vibrational features smear out step by step.

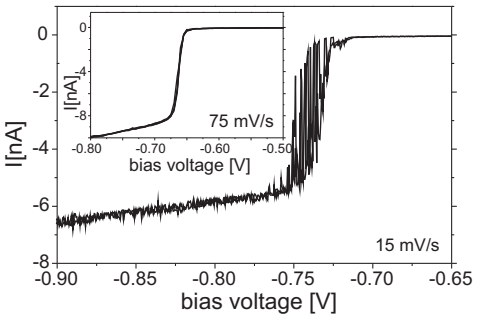

FIG. 4: I-V measurements that show high fluctuations at the onset of current when lowering the scanning speed from 75 mV/s (inset) by a factor of five.

the resolution of vibronic excitations, in the first measurement three distinct excitations can be resolved, the second shows only two of them, in the third only the first appears clearly while the fourth does not reveal a clear substructure anymore. Since only the blockade region is enlarged and the junction is essentially unaltered in the process, the reason for the smearing of the vibronic excitations should be the larger electric field. The change in electrode spacing is estimated to about 13 pm, and can be neglected compared to the length of the molecule of 2 nm. Only a slight modification is seen in the first vibronic peak that changes the amplitude relative to the others, but the increasing smearing towards higher bias is the most obvious effect. Within the model, this can be assigned to a change in the electron-vibration coupling parameters. However, the nearly ubiquitous observation of smeared-out peaks at higher bias is rather likely to be explained by an additional smearing mechanism.

At this point, a detailed analysis of the first peak with respect to fluctuations is desirable. We show in Fig. 4 a relatively sharp onset of current in the high bias regime (≈ -700 mV). An apparently stable current-voltage characteristic is observed at a measurement speed of the voltage sweep of 75 mV/s (inset). Repeating the measurement at a slower speed of 15 mV/s in this case (not always) leads to high current fluctuations. We conclude that there are instabilities of the IV characteristics, which are associated to structural reconfigurations, given the slow timescales.

In order to get a deeper understanding of the timescales of these fluctuations noise measurements are carried out parallel to the I-V-characteristics at a similar molecular contact. Fig. 5a shows the spectral noise density as a function of voltage for three chosen frequencies as well as the differential conductance (red curve) at the first peak with an FWHM of ≈ 150 mV. The current noise is low in the blockade region, and increases by four orders of magnitude close to the maximum of the conductance peak. It then decreases again by two orders of magnitude after the first peak. This is a finding of high importance for the understanding of the first peak, and is not anticipated by the resonant tunnelling models. A closer look reveals that the maximum of the noise is actually at lower bias than the maximum of the conductance peak, in particular at lower frequencies. In other words, the fluctuations are maximum when the current starts to flow. This reminds a model proposed by Koch et al. [14]. The authors considered an increased Fano factor (i.e. shot noise level) in the weak coupling regime, with a Franck-Condon weighted electron-vibration coupling. The basic idea is that in the transport model tunnelling is energetically allowed when the first electronic level is reached, but suppressed due to a weak wave function overlap (Franck-Condon blockade). When reaching a bias which allows also to excite a vibration, the molecule starts to vibrate as a consequence of a first tunnelling event, and under some realistic assumptions a stronger overlap will allow more electrons to tunnel through the junction. In their model, avalanche-like amplification of the current occurs, and with a certain probability the current breaks down to zero after a while. These statistics leads to giant shot noise signals at the onset of current flow. Although the experimental situation is more complex than this theoretical and, in addition, is limited to shot noise rather than configurational noise, we think that some essential ideas are also valid for single-molecule junctions in the high-bias regime. We consider the case that the onset of current triggers configurational fluctuations. One may suspect that there exist field-sensitive bistabilities, which need a certain field strength to be active. The onset of current and eventually of first vibrational excitations may be the trigger of further field-induced structural reconfigurations, which appear as low-frequency noise or instabilities. Alternatively, a deformation of the molecule might act on the threshold value itself, providing a situation similar to a polaron instability [3, 15, 16]. As we know, the average charge on the molecule changes when the current sets in. This may induce a structural change, or may create structural bistabilities, also on low timescales. Common to these illustrative considerations

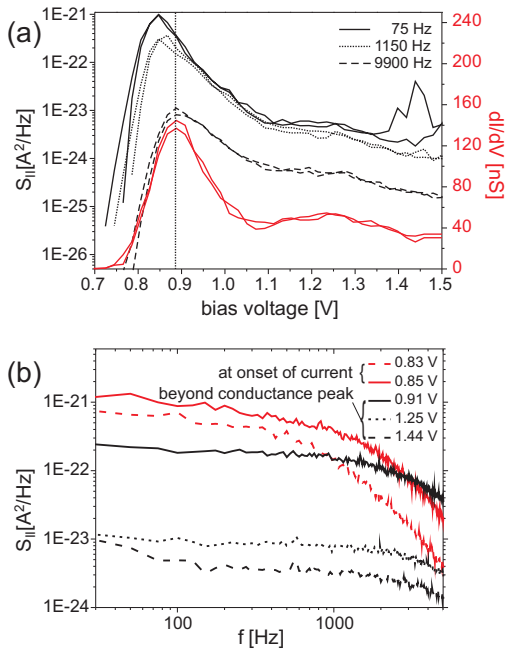

FIG. 5: (a)Spectral noise density at three different frequencies and $\mathrm{d}I/\mathrm{d}V$ curve (red) at the first conductance peak. At the onset of current the noise is several orders of magnitude enhanced. (b) Noise spectra at the onset of current (red) and beyond the conductance peak (black) show different frequency dependence (f^{-2} vs. f^{-1}) above 1 kHz.

is the observed phenomenon that the onset of current triggers reconfigurations, accompanied by large fluctuations. When further increasing the bias the system undergoes a strongly fluctuating regime, with first a maximum in the noise signal and subsequently a maximum in $\mathrm{d}I/\mathrm{d}V$. Beyond the two maxima, the current reaches a higher level (similar to the resonant tunnelling model), whereas the noise is reduced. This indicates an approximately steady state. The noise measurements indicates that the physics of the first peak is much more complicated than its similarity to the resonant tunnelling model suggests.

Some further information can be extracted from the frequency dependence of the current noise density (Fig. 5b). The presented curves at five different voltages split into two pairs, the red curves at the onset of current, and the black ones for bias voltages beyond the maximum of the differential conductance. The first pair approximately follows a decay $\propto f^{-2}$, whereas the rest resembles more to a f^{-1}-dependence. While the higher exponent is ascribed by a simple Lorentz oscillator model to a single fluctuator [17], the latter can be explained by the superposition of several oscillators with uniformly distributed time constants [18, 19].

Hence, there are two different origins of noise identified. On the one hand the first electronic transition is accompanied by one dominating bistability of the molecular contact configuration. This was surprising to us and may point to an intrinsic effect, for example the polaron model, rather than to fluctuations in the gold leads. Beyond the peak, many fluctuators are active. Hence, the first current plateau should be understood as a dynamic interplay of charge flow and dynamical reconfigurations of the molecule. This picture goes well beyond the resonant tunnelling model.

Altogether, from many experiments with more than ten conjugated molecules and from detailed calculations, we receive the following picture of charge transport through single molecules: The purely electronic transmission is accompanied by distinct vibrational resonant conduction channels. At low voltage, these smear out due to finite temperature and for a broad distribution of vibronic modes leading to a rather broad peak. More complicated physics happens at even higher electric field. The transition from the blockade regime to the conducting regime shows strong configurational fluctuations, with a noise maximum before the maximum of the differential conductance. At these higher bias thresholds, as soon as current flows in a molecule, strong structural fluctuations are associated to it. Hence the similarity of the IV characteristics to the resonant tunnelling model may be rather fortuitous at higher bias.

We acknowledge funding of the DFG in the framework of the SPP 1243 "Quantum transport on the molecular scale". The work was carried out in the Cluster of Excellence "Engineering of Advanced Materials"at the Friedrich-Alexander-Universität Erlangen-Nürnberg.

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